

OFFICE OF NAVAL RESEARCH

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Robert Nowak

Pulse Voltammetric Characterization of Biocorrosion Processes

by

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13. ABSTRACT (Maximum 200 words) <p>The work on anodization of copper electrodes for the first time presented a closed-form solution to the problem of relating the distribution of products of metal oxidation to the potential of the metal. In addition it presented a new method, based on normal pulse voltammetry at microelectrodes, for the determination of the stability constants of complexes, especially appropriate for the formation of chloride complexes in seawater. This work also identified and treated qualitatively the problem of coupled migration, diffusion, and complex formation in seawater.</p> <p>The work on thermoconvection provided a quantitative treatment of the effect of temperature differences on the rate of metal dissolution or deposition. Enhanced rates due to thermoconvection are observed for both negative and positive gradients, and the gradient has a strong qualitative influence on the potential dependence of the current. Thermal gradients are common in copper-containing equipment in contact with seawater. This work explains the consequence of such gradients.</p>				
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- a. Number of papers submitted to refereed journals, but not published: 0  
b. + Number of papers published in refereed journals (for each, provide a complete citation): 2  
c. + Number of books or chapters submitted, but not yet published: 0  
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e. + Number of printed technical reports/non-refereed papers 0  
(for each, provide a complete citation): 0  
f. Number of patents filed: 0  
g. + Number of patents granted (for each, provide a complete citation): 0  
h. + Number of invited presentations (for each, provide a complete citation): 17  
i. + Number of submitted presentations (for each, provide a complete citation): 5  
j. + Honors/Awards/Prizes for contract/grant employees (list attached): 9  
(This might include Scientific Society Awards/Offices, Selection as Editors,  
Promotions, Faculty Awards/Offices, etc.)  
k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported  
during this period, under this R&T project number: 4.55  
Graduate Students: 0.9  
Post-Doctoral Associates: 3.4  
including the number of:  
Female Graduate Students: 2.5  
Female Post-Doctoral Associates: 0  
the number of:  
Minority\* Graduate Students: 0  
Minority\* Post-Doctoral Associates: 0  
and the number of:  
Asian Graduate Students: 0  
Asian Post-Doctoral Associates: 0  
l. Other funding (list agency, grant title, amount received this year, total amount, period of performance  
and a brief statement regarding the relationship of that research to your ONR grant)  
+ Use the letter and an appropriate title as a heading for your list, e.g.:  
b. Published Papers in Refereed Journals; or  
d. Books and Chapters published.

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\* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

**OFFICE OF NAVAL RESEARCH  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT**

a.     Number of Papers Published:           2

Anodization of Copper Microelectrodes in a Complexing Medium. Determination of Stability Constants of Products, Orr, James T., Osteryoung, Janet G., *Analytical Chemistry* 67, 2714-2722 (1995).

Thermoconvection-Enhanced Deposition of Copper, Isaev, N., and Osteryoung, Janet G., *Journal of the Electrochemical Society* 142, 4103-4107 (1995)

h.     Number of Invited Presentations:       17

From Azobenzene to Zinc, Tennessee Tech Chapter-Sigma Xi, Cookeville, TN, October 1993.

Electroanalytical Chemistry of the Environment, Department of Chemistry, Tennessee Tech, Cookeville, TN, October 1993.

Modern Voltammetry, Kansas City Section, Kansas City, MO

Modern Voltammetry, Southeast Kansas City Section, Pittsburgh State University, Pittsburgh, KS

Modern Voltammetry, Wichita Section, Wichita, KS

Women in Analytical Chemistry, 76th Canadian Society for Chemistry Conference, Sherbrooke, Quebec, Canada, June 1993

Pulse Voltammetry, Seventh National Conference on Analytical Chemistry, Rio de Janeiro, Brazil, September 1993

Applications of Square Wave Voltammetry, Department of Chemistry, University of South Carolina, October 1993

Modern Voltammetry, Kansas State University Section, Kansas State University, Manhattan, KS

Electrochemistry: Current and Future, Roche Carolina Symposium, Francis Marion University, Florence, SC, May 1994

Electroanalytical Chemistry of the Environment, Spelman College, Atlanta, GA, July 1994.

Mechanisms and Analytical Applications of Surface Processes at Electrodes, Georgetown University, Washington, DC, September 1994.

Square-Wave Voltammetry for Studies of Mechanism, W. Virginia University, Morgantown, WV, September 1994.

Modern Electroanalytical Chemistry, 45th Annual Meeting of the International Society of Electrochemistry, Porto, Portugal, September 1994.

Square-Wave Voltammetry, U. of Wisconsin at Milwaukee, Milwaukee, WI, October 1994.

Modern Electroanalytical Chemistry, The Mississippi Chemical Company Lectureship, University of Mississippi, Oxford, MS, October 1994.

Analytical Applications of Pulse Voltammetry, American Chemical Society, Washington Capitol Section, Washington, DC, November 1994.

i. Number of Submitted Presentations: 5

Computational and Experimental Aspects of Copper Anodization, NC ACS Sectional Conference, NCSU, April 1994 (with J. T. Orr)

Thermoconvection-Enhanced Deposition-Dissolution of Copper, 185th Electrochemical Society Meetg, San Francisco, May 1994 (with Nick Isaev)

Anodic Reactions of Copper; poster, 45th Annual Meeting of the International Society of Electrochemistry, Porto, Portugal, September 1994 (with J. T. Orr and K. Wikiel).

Determination of Formation Constants of Products of Copper Anodization, 186th Meeting of The Electrochemical Society, Miami Beach, FL, October 1994 (with J. T. Orr and K. Wikiel).

Interdigitated Array Electrode Sensor for Copper Species, 109th Sectional Conference, North Carolina Section, American Chemical Society, Chapel Hill, NC, April 1995 (with J. Urbanik).

j. Honors/Awards/Prizes (J. Osteryoung): 10

Chair-elect and Program Chair, Analytical Division, ACS, 10/1992-9/1993

Scientific Advisory Council, National Institute of Statistical Sciences, 1993-

Chair, Analytical Division, ACS, 10/1993-9/1994

Director, Chemistry Division, National Science Foundation, 1994

Immediate Past-Chair, Analytical Division, ACS, 10/1994-9/1995.

Participant, Electrochemical Sciences Program Review, Office of Naval Research, January, 1995.

Vice-Chair, Gordon Research Conference on Electrochemistry, January 1995.

Program Committee, Council on Chemical Research, 1994-1995.

Chair, Gordon Research Conference on Electrochemistry, 1996.

American Chemical Society Analytical Division Award in Electrochemistry, August, 1996.

1. Other Support:

Agency, Grant Title	Amt. This Year \$k	Total Amount \$k	Period
ARPA, Technology Reinvestment Program	175,000	349,203	8/15/94- 12/31/96

This project involves advanced plating systems. In the course of these studies, we have considered systems in which migration and homogeneous equilibria are involved, which makes them formally equivalent to the problem of anodization of copper in seawater.

NSF, Analytical Pulse Voltammetry	102,000	389,000	3/1/92- 2/28/97
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The two main topics are studies of transport in polyelectrolyte and other systems by voltammetry at microelectrodes and the analytical chemistry and reduction mechanisms of adsorbates on mercury electrodes. Neither of these projects is directly related to the ONR grant, but both provide fundamental results which support the ONR-funded work. In particular, we are gaining valuable experience with polyelectrolytes and are exploring the problem of coupled migration and homogeneous equilibria.

NSF, U.S. Poland Cooperation in Analytical Pulse Voltammetry	11,000	32,300	9/1/92- 1/31/96
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This grant supports travel and visiting scientists for collaboration with Z. Stojek of the University of Warsaw on the main NSF grant.

NSF, Visiting Committee to Poland	26,328	39,505	3/1/94- 8/31/95
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This grant supports assessment of chemical research in Poland through a visit and subsequent report.

Importance of Publications:

The work on anodization of copper electrodes for the first time presented a closed-form solution to the problem of relating the distribution of products of metal oxidation to the potential of the metal. In addition it presented a new method, based on normal pulse voltammetry at microelectrodes, for the determination of the stability constants of complexes, especially appropriate for the formation of chloride complexes in seawater. This work also identified and treated qualitatively the problem of coupled migration, diffusion, and complex formation in seawater. Most studies of corrosion products are qualitative. This lengthy paper lays the foundation for quantitative studies.

The work on thermoconvection provided a quantitative treatment of the effect of temperature differences on the rate of metal dissolution or deposition. Enhanced rates due to thermoconvection are observed for both negative and positive gradients, and the gradient has a strong qualitative influence on the potential dependence of the current. Thermal gradients are common in copper-containing equipment in contact with seawater. This work explains the consequence of such gradients.

Importance of Award:

The Award for Electrochemistry of the Analytical Division of the ACS signifies the general regard in which the above work is held.